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Behaviour of Heavy Metals During
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REFERENCE 2

THE BEHAVIOR OF HEAVY METALS DURING LANDFILL DISPOSAL OF HAZARDOUS WASTES

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ABSTRACT

Research investigations on the production and control of leachates from simulated landfill columns operated with leachate recycle and containing residential-type solid waste codisposed with heavy metal sludges are discussed with emphasis on the chemistry of the leachates generated and the reactivity and fate of the heavy metals contained therein. Changes in leachate ionic strength and resulting activity coefficients are presented to indicate that activity corrections in the metal sludge-containing columns decreased from about 0.8 for monovalent ions, to 0.4 for divalent ions, and to 0.12 for trivalent ions. The impact of these decreases in activity are interpreted in terms of probable chemical and biological interactions within the columns and leachate.

Heavy metal solubilities are shown to depend on the precipitating capability of the sulfide present under the reducing conditions of the landfill environment, and the mobilization effect of humic acids present in the leachates and acting as complexing agents. A strong positive correlation between aromatic hydroxyl concentrations and several of the heavy metals in the leachates was found.

Collectively the data emphasize the ability of leachate recycle to moderate and provide equilibration between leachates and solid waste constituents. The significance of this in terms of both leachate quality and predictability is discussed within the perspective of landfill management practices.

INTRODUCTION

The heterogeneity of waste materials deposited in landfills will be reflect in the production of leachates of extraordinary chemical complexity. As landfills mature and leachates form, all processes which control chemical composition and the distribution and nature of dissolved species in the leachates will undergo complicated sequences of interrelated changes. Accordingly, available free oxygen will be rapidly consumed with consequent development of anaerobic conditions. These conditions will then favor further microbial conversion of organic and inorganic materials, i.e., the generation of organic acids and their conversion to methane and carbon dioxide, the reduction of sulfates to sulfides, and the production of reduced forms of metals such as Fe^{+2}, Cr^{+3}, Mn^{+2} and Hg_2^{+2}. However, the generation of such species might also be inhibited or prevented altogether by the presence of materials toxic to the same organisms primarily responsible for their formation. Such inhibition may suppress a process permanently, delay its initiation or, where appropriate feed-back mechanisms exist, lead to cyclic behavior. Collectively, knowledge of these factors will not only have a major impact on understanding the distribution, speciation and mobility of heavy metals and other leachate constituents, but will greatly enhance the predictability of leachate generation and

migration in time and space and thereby the adequacy of design and management of landfill disposal sites.

The objective of the research reported here was to extend previous investigations on the reactivity and fate of potentially toxic heavy metals during landfill disposal of solid and hazardous wastes. This objective was accommodated with further investigations of the codisposal of residential-type municipal solid wastes and metal plating sludges in simulated landfill columns operated with leachate containment, collection and recycle. The experimental strategy used included a chemical characterization of the leachates generated, an identification of the distribution and speciation of toxic heavy metals in the leachates, and an assessment of the factors controlling heavy metal solubility and mobility.

INITIAL CONSIDERATION

Initial studies have addressed the chemical complexity of leachates generated from the simulated landfills[1,2]. Short and long-term changes in many of the physical and chemical indicator parameters were measured and recorded including variations in pH from distinctly acid to slightly alkaline conditions and in oxidation-reduction potentials from positive to negative. These two parameters were given pivotal roles in determing the inherent chemical form and reactivity of various leachate constituents. In addition to these measurements, concentrations of several potential inorganic and organic complexing agents have been determined including chloride, sulfate, ammonia, humic substances, amino acids and volatile acids. All of these leachate parameters affect or are reflected in the ionic strength which, in turn, determines the extent to which chemical activity will cause a deviation in measured concentrations from the true concentration and reactivity of constituent species.

To further explore and evaluate the reactivity and fate of heavy metals during landfill disposal of solid wastes, operation of the four simulated landfill columns, described in detail previously[1,2] and illustrated in Figure 1, was continued. The control column (Column 1), charged with residential-type solid waste, and the test columns (Columns 2, 3 and 4), also including varying quantities of metal plating sludge of quantity and composition given in Table 1, continued to receive moisture from rainfall or tap water addition to permit leachate production and recycle.

During the 711-day operation of these columns, both dilution and evaporation of leachate occurred. This resulted in periods during which there was insufficient leachate available to permit recycle on a continuing basis. One such period of approximately 150 days, during which leachate could not be withdrawn for analysis, was incurred. While this resulted in an interruption in the analytical results, it did provide an opportunity to examine leachate characteristics and behavior during low leachate production periods analogous to those encountered in actual practice. The dry and often warm to hot weather conditions causing the substantial evaporation losses of leachate increased the concentrations of high solubility conservative species such as chloride and sodium. This reduction in volume coupled with an increase in constituent concentrations had a noticeable effect on microbial activity and ionic strength, both of which will be emphasized in the ensuing discussion.

ANALYTICAL METHODS

Leachate from the columns was analyzed for inorganic components by conventional techniques; metals by digestion and atomic absorption spectroscopy, chloride and sulfide by electrochemical techniques, and ORP, pH and conductivity by the usual instrumental methods. Analyses for the organic constituents discussed herein involved direct aqueous injection gas chromatography for volatile organic acids and the Folin-Dennis method for aromatic hydroxyl groups[3]. For equilibrium analysis, constants were obtained from the classic compilations of Sillen and Martel[4,5].

ANALYTICAL RESULTS

Conductivity, Ionic Strength and Activity

As has been reported previously[2], the high ionic strength of leachates and its relationship to chemical activity represents a significant factor in considering the fate of leachate constituents from

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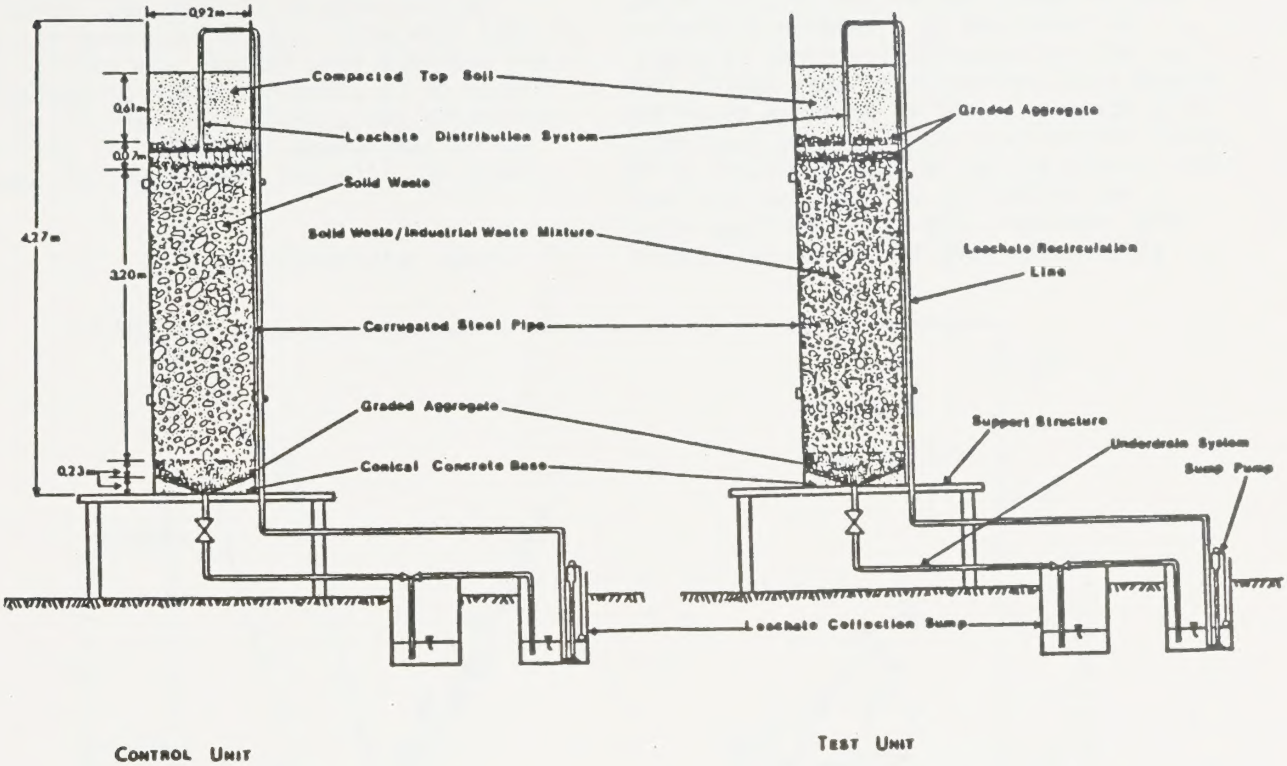

Figure 1. Simulated Landfill Columns with Leachate Collection and Recycle

TABLE 1. CHARACTERISTICS OF METAL SLUDGE USED IN COLUMN INVESTIGATIONS

Moisture Content, %		84.7
Volatile Solids, %		24.6
Zinc, mg/kg dry		317,000
Chromium, mg/kg dry		21,000
Nickel, mg/kg dry		400
Cadmium, mg/kg dry		13,100
Copper, mg/kg dry		185
Iron, mg/kg dry		94,000
Sulfate, mg/kg dry		30,000
Sludge Added:	Column 2, kg	33.6
	Column 3, kg	65.8
	Column 4, kg	135.2

land disposal sites. To illustrate this influence, the specific conductance of leachate generated in four simulated landfill columns was plotted with time and the corresponding ionic strength, μ, in Figure 2. In this determination, μ was estimated according to the linear approximation developed by langelier[6], Russell[7] and Lind[8], or

$$\mu = 1.6 \times 10^{-5} \times \text{conductivity, } \mu\text{mho.}$$

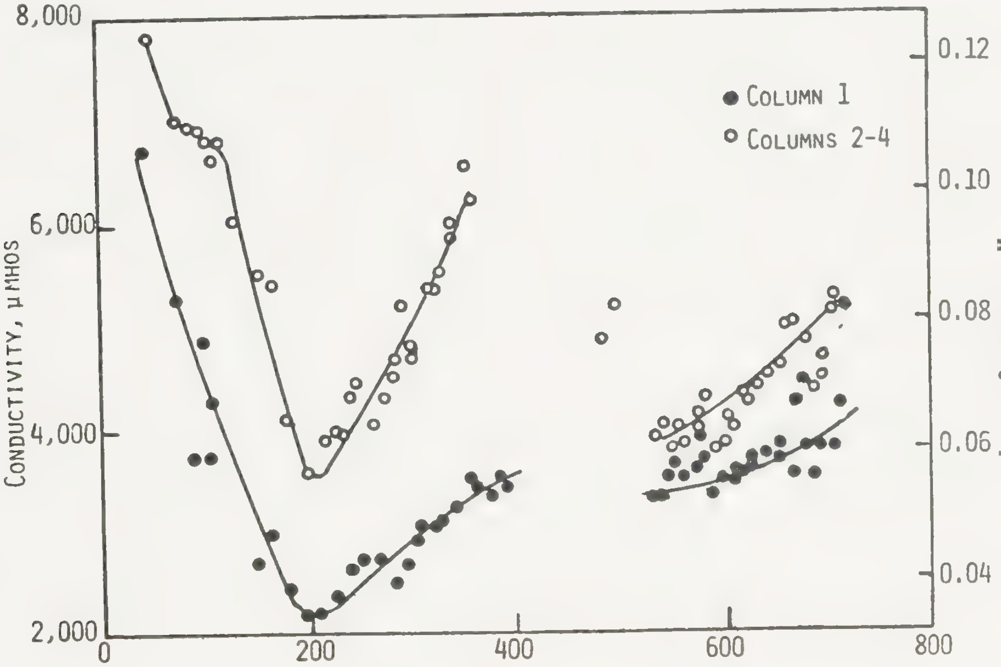

Figure 2. Ionic Strength and Conductivity as a Function of Time Since Loading Columns.

For comparison with the control column (Column 1), the ionic strength values for the test Columns 2-4 were consolidated, since no significant systematic differences were found between the leachates from the three columns containing metal sludge. These latter ionic strengths were consistently higher and reflect the presence of leachate inorganic species contributed primarily by the metal sludge contained in the three test columns. It is also significant that the differences in conductivity/ionic strength were dimishing during the latter stages of the study, thereby indicating that excess leachable constituents in the metal sludge-bearing columns may have been approaching depletion or some type of equilibrium conditions.

Temporal trends of conductivity/ionic strength are clearly related to the initial composition of the wastes placed in the respective columns. As presented in Figure 2, the first 200 days for the control column were characterized by a smooth and rapid decrease in ionic strength with a decrease of about 70% from initial levels. While simple washout of mobile conservative ions such as chloride and sodium was a major contributor to this decrease, biological conversion of such potentially ionic species as sulfate and organic acids was also considered to be important to the reduction in ionic strength. Leachate from the metal sludge-bearing columns generally behaved in a similar fashion except that a distinct pause was noted in the decrease of ionic strength between 50 and 150 days. This pause has been ascribed to a period during which heavy metal inhibition was limiting the biologically mediated reduction in ionic strength. It should also be emphasized that the resumption of the rapid decrease in ionic strength for Columns 2-4 corresponded closely to the reduction in zinc (Figure 3), a measurable and reliable tracer of heavy metal contamination in the leachate, to levels below about 50 mg/l. This tended to support the premise that biological activity significantly influenced decreases

in ionic strength during the early stages of the investigations.

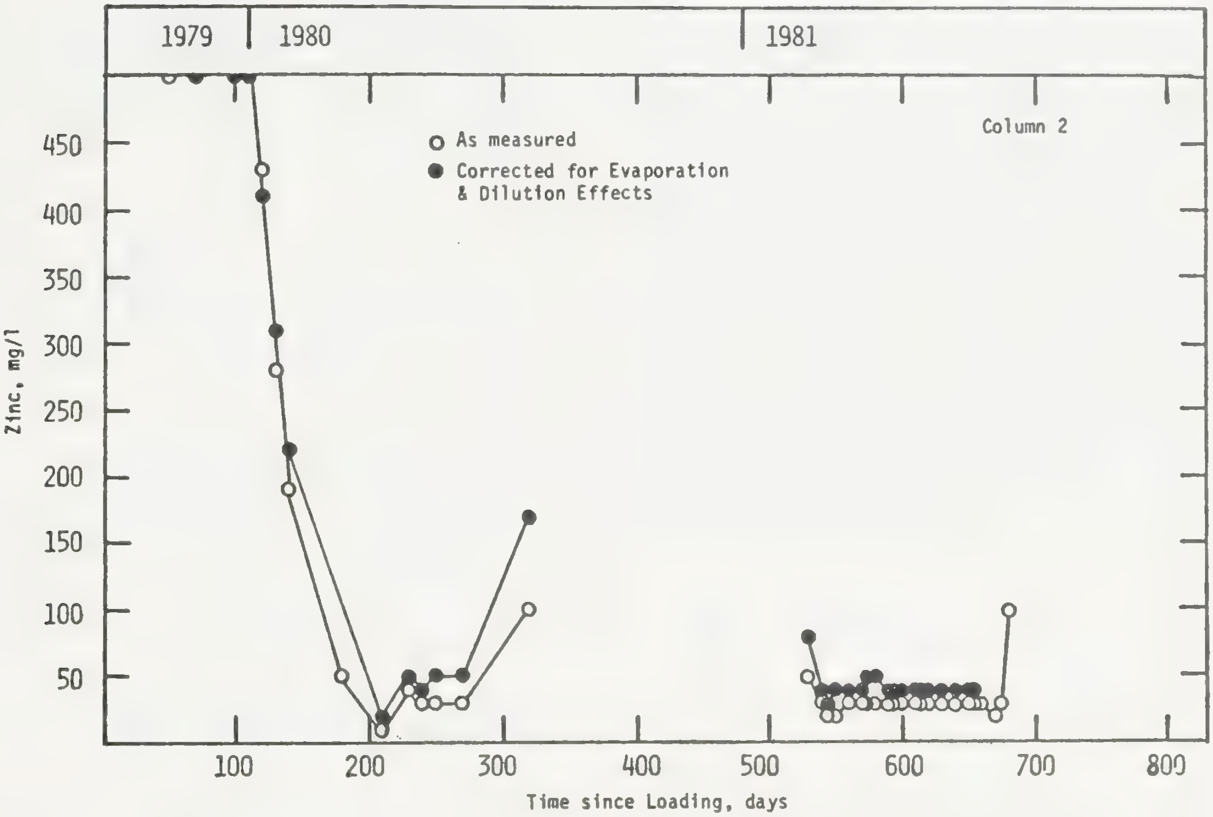

Figure 3. Concentration of Zinc in Column 2 as a Function of Time Since Loading Columns

Following the initial decrease in ionic strength, a substantial increase was observed between 200 to 400 days for both the control and the metal sludge-containing columns. The leachate from the metal sludge-containing columns recovered almost 70% of the initial decrease, while the recovery for the control column was only about 30% of the initial decrease in ionic strength. This increase in ionic strength was considered dependent on a corresponding pH increase with its attendant ionization of organic acids. (Supplemental data on elevated volatile acid levels in the leachate from Columns 2-4 yielded a far greater concentration of anions in response to a pH increase than observed for the control column.) This accumulation of volatile acids was again likely due to inhibition of their biological conversion to methane caused by the excessive concentrations of heavy metals in the leachate from Columns 2-4.

Ionic strength data collected between the resumption of leachate generation on Day 529 and termination of sampling at Day 711 show some overlap between the control column ionic strengths and those of the metal sludge-containing columns. A gradual increase, amounting to about 25% of the initial value, was observed for all columns during this period while the pH remained relatively constant. These analytical data tend to reflect the effects of evaporation and attendent concentration of leachate constituents and ionic strength for this stage of the investigations.

To underscore the importance of changes in leachate ionic strength, activity coefficients have been computed for mono-, di- and trivalent ions as a function of time and are presented in Figure 4, again consolidating data for Columns 2-4. The activity coefficients indicated in this figure were calculated by means of the extended DeBye-Hückel equation[9] or

$$-\log \gamma_i = \frac{0.5\ Z^2 \mu^{\frac{1}{2}}}{1 + \mu^{\frac{1}{2}}}$$

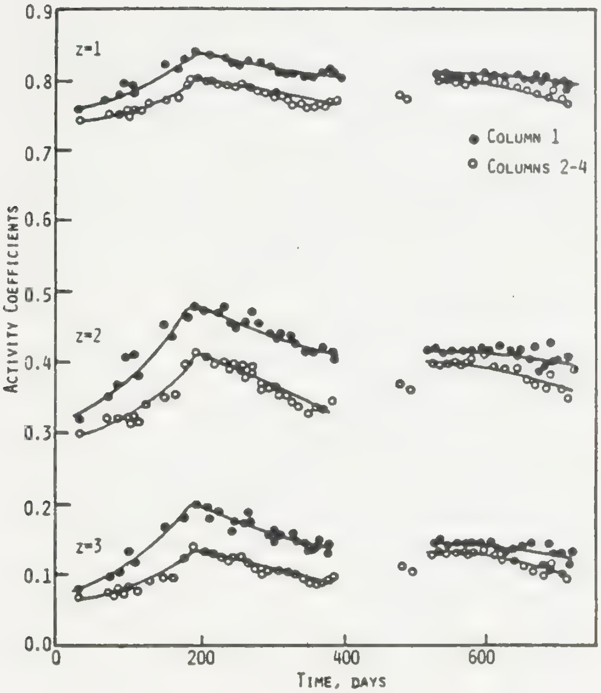

Figure 4. Activity Coefficients as a Function of Time since Loading Columns

Inspection of these data indicates a distinct inverse relationship to ionic strength. Moreover, the activity correction coefficients are clustered around 0.8 for monovalent ions, 0.4 for divalent ions, and 0.12 for trivalent ions. The relative magnitude of these coefficients and their important impact on the behavior of ionic species in leachate have also been discussed in detail previously[2].

Solubility Control in Leachates

The factors controlling metal solubility in landfill leachates include: the concentrations of potentional precipitant species such as hydroxide, carbonate and sulfide; the existence of complexing agents which will tend to increase metal solubility; and, the pH-ORP relationships which will impact on both heavy metal and precipitant speciation.

Hydroxide. Previous investigations[2] have indicated that, with the exception of trivalent chromium which is controlled by the solubility of its hydroxide, solubility control will be only rarely vested in the solubility of metal hydroxides in normal landfill leachates.

Carbonate Species. The decomposition of organic matter in landfills provides a continuing source of inorganic carbon. Examination of leachate total inorganic carbon data from the landfill columns indicated that this parameter showed random rather than systematic variations and averaged about 5.5 mM. Using this as a typical value for total carbonate species in the leachate from the columns, a pH-pC diagram for carbonate CO_3^{-2} has been constructed in Figure 5. Several heavy metal carbonates and basic carbonates have the potential to control the solubility of metals in those instances where sulfide may not be present; solubility of the heavy metals then will be inversely dependent on the prevailing carbonate concentration as shown in Figure 5.

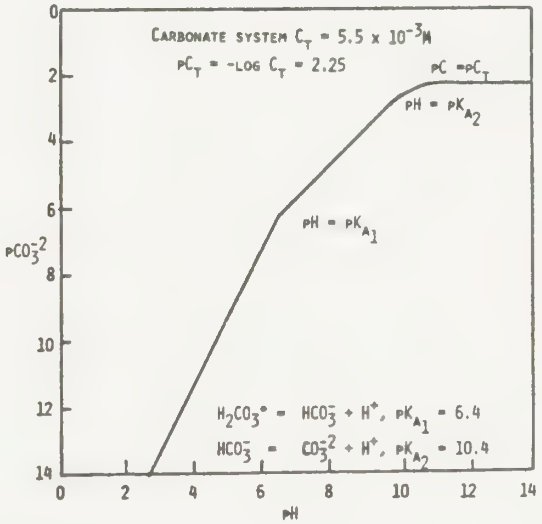

Figure 5. pH - pCO_3 Distribution Diagram for Carbonate in Leachates

Sulfide. Analytically, sulfide measurements present complications. Unlike carbonate, which is generally a modest precipitant at pH 8 or lower, sulfide, S^{-2}, is such a powerful precipitating agent that, even at low pH values and very low sulfide concentrations, most of the sulfide generated will be bound to heavy metals as metal sulfides. As an example, the measured total dissolved sulfide concentrations in the leachates

from the test columns have averaged approximately 0.5 mg/ℓ or 1.6×10^{-5} M(1.8×10^{-12} M S^{-2} at pH 7). Since the solubility product of ZnS is 10^{-25}, the actual solubility of zinc was 6×10^{-14} moles per liter. Thus, the presence of even sub-milligram per liter levels of total dissolved sulfides at relatively low pH values implies the presence of a strong sulfide precipitating capacity.

Complexing Agents. The role of complexation in complicated matrices such as leachates involves considerable uncertainty. Complexing agents, by converting sparingly soluble salts to soluble complexes, can counteract the impact of precipitant ions and thus increase the solubility of metals. Previously reported investigations have discounted significant complexation between even the most abundant inorganic ligands, such as chloride and sulfate, and any of the metals common to the metal sludges used in this research[2]. Likewise, with one important exception, identified organic species including carbonyls, carbohydrates and volatile acids are simply too weak as complexers to be of substantial influence in heavy metal solubilization. The one exception is represented analytically in these studies by the aromatic hydroxyl (ArOH) compounds, a measure of the moderate to high molecular weight tannin and humic acid substances. Such compounds are of pivotal importance in the control of solubility of certain heavy metals.

Oxidation-Reduction Potentials (ORP). The ORP of a leachate will have considerable impact on its chemical speciation. Thus, the reducing conditions to be expected in a landfill environment will favor the biological conversion of sulfate to sulfide and the production of methane from organic substrates. In addition, the conversion of Fe^{+3} to Fe^{+2} and Cr^{+6} to Cr^{+3}, with consequent major impact on solubility, will be favored.

While sampling and analytical difficulties limited exact ORP determinations, the presence of significant concentrations of reduced iron and sulfide ions provided confirmation of the presence of highly reducing conditions within the landfill columns and leachates. Figure 6 is a pH-pε diagram for the sulfate-sulfide system and indicates conditions necessary to favor the presence of sulfide. Clearly, oxidation-reduction potentials within the landfills and leachates must be strongly reducing since sulfides predominate at ORP values no more positive than -450 mV relative to the saturated calomel electrode (E_c) at 25°C.

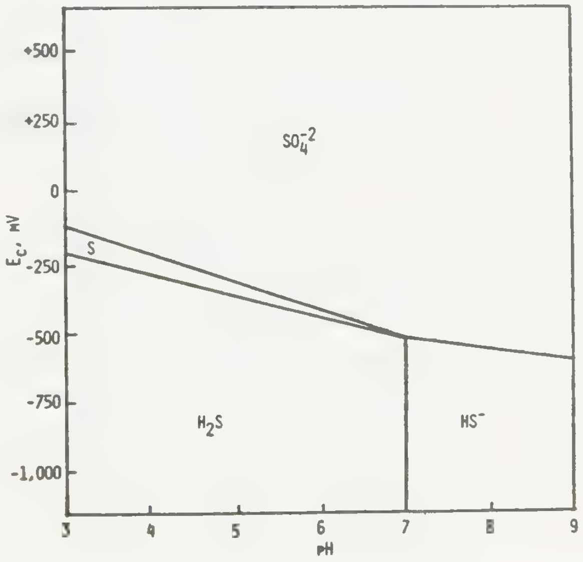

Figure 6. pH-E_c Diagram for the Sulfate-Sulfur-Sulfide System

Another factor of importance in the sulfate-sulfide system is biological activity. Since most sulfate reduction in leachates of organic waste origin is biologically mediated, high levels of inhibitory materials such as heavy metals may preclude sulfate reduction even under favorable pH-pε conditions. Similar considerations apply to methane formation with requisite ORP and pH values of about -500 mV E_c and 7.0, respectively.

Heavy Metal Solubility Control in Leachates

Among the metals commonly regarded as heavy metals, routine monitoring was conducted during these studies for cadmium, chromium, copper, iron, manganese, nickel and zinc. Due in part to the composition of the admixed heavy metal sludges and to the general solubility behavior of these metals, the only elements measured with any analytical consistency in the leachates were cadmium, nickel and zinc which originated primarily from the metal sludge.

Since zinc was the major heavy metal in the admixed sludge (Table 1) and attained the highest concentrations of any of the heavy metals in the leachates, an initial examination of the solubility behavior of this element provides significant direction regarding solubility control in landfill leachates. Shown in Figure 7 are predicted pH-pC diagrams for zinc solubility based on hydroxide control and on average concentrations of available carbonate and sulfide in the leachates.

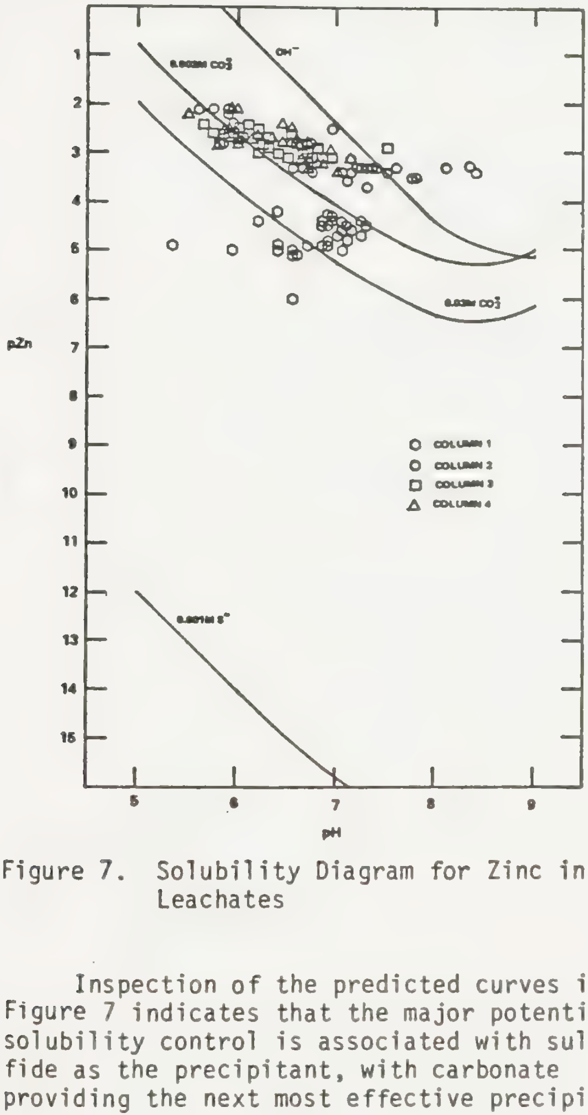

Figure 7. Solubility Diagram for Zinc in Leachates

Inspection of the predicted curves in Figure 7 indicates that the major potential solubility control is associated with sulfide as the precipitant, with carbonate providing the next most effective precipitant and hydroxide being the least likely solid zinc species in these leachates. By plotting the actual measured pZn versus pH values from these studies also on Figure 7, certain observations can be made. First, the three metal sludge-laden columns indicated no obvious differences in the pZn-pH values. Apparently, all three of these columns were at saturation in terms of zinc and the leachate environment. Secondly, while these data tend to cluster mainly between the carbonate and hydroxide solubility curves, those at high pH exceed the solubility limits of the hydroxide solubility control. Therefore, whatever solid phase is controlling zinc solubility, there is superimposed upon this system some factor which acts to increase solubility. Although not as dramatic, this influence appears also to be exerted on the data for the control column. The most obvious explanation is the presence of some complexing agent.

As indicated previously, the most likely complexing agents in leachates are the moderate to high molecular weight phenolic compounds arising from the decomposition of plant materials and generally referred to as humic substances. The aromatic hydroxyl (ArOH) groups measured in the leachates from these studies provided an effective measure of these substances. The ArOH levels were generally high during the initial phases of leachate generation in all four columns and decreased rapidly to essentially constant levels during the mid-period. While this constant ArOH level was maintained for the control column and for Column 2 during the balance of the studies, a later increase in ArOH for Columns 3-4 was noted. This probably reflected a sequence of microbial inhibition followed by acclimation in the metal sludge-bearing columns.

In order to assess the relationship between ArOH and soluble zinc concentrations, a plot of Zn versus ArOH is presented in Figure 8 where it is evident that a marked positive correlation between aromatic hydroxyl and zinc solubility exists. This strongly supports the concept that humic substances, as quantified by the aromatic hydroxyl analysis, played a major role in zinc solubility in these leachates. Moreover, in an effort to arrive at an estimate of the magnitude of the Zn-ArOH complex interaction, several assumptions have been applied, including the premise that fundamental solubility control lies in the domain of sulfide solubility and that a polynuclear complex between Zn^{+2} and the ligand, L, exists. Using these assumptions, the following equilibria can be formulated:

$$2ZnS + L \rightleftharpoons Zn_2L + 2S^{-2} \qquad \log K_s = -26.2$$

$$2Zn^{+2} + 2S^{-2} \rightleftharpoons 2ZnS \qquad 2 \log \frac{1}{K_{sp}} = +49.6$$

or;

$$2Zn^{+2} + L \rightleftharpoons Zn_2L \qquad \log \beta = +23.4$$

where,

L = some complexing ligand. [L] = 40 M

K_s = solubility of solid ZnS to yield Zn_2L

K_{sp} = solubility of solid ZnS to yield Zn^{+2} and S^{-2}

β = formation constant of complex from Zn^{+2} and Ligand

The resulting formation constant is in reasonable agreement with Reuter's estimate of +20 for the log of the formation constant of a heavy metal-humic acid complex[11].

Based on the promising results with zinc, similar plots for cadmium, manganese and nickel versus ArOH have been prepared and are presented in Figures 9 through 11. Although these data are more scattered than in the case for zinc, the positive correlation between the respective metals and ArOH is again obvious. The tendency toward a leveling of metal concentrations at high ArOH values may suggest that for some metal species and ArOH concentrations, as the metal-ArOH complex increases in concentration, some competing reaction comes into play to counteract the complexing effect of the humic substances. Over the concentration ranges observed, no such influence was detected in the case of zinc or cadmium. This similarity between zinc and cadmium was not unexpected since these metals classically show very similar chemical behavior.

Metal Behavior and Recycle

The results reported herein have important implications with regard to the use of leachate recycle as a solid waste management option at landfill disposal sites. Since one of the objectives of leachate recycle is to provide an increased opportunity for contact between the liquid and solid phases within a landfill, thereby permitting the liquid phase to attain the closest approach possible to equilibrium in terms of the chemical, biological and physical interactions, evidence of improved equilibration attained by recycle strongly enhances the relative merits of this process in terms of both fundamental process understanding and application. That leachate recycle should have beneficial effects on the predictability of leachate quality and the reduction in potential for environmental impairment has been emphasized previously[1,2]. By increasing effective contact and homogeniety, conversion efficiency tends to be substantially increased over single contact systems, i.e., systems without leachate containment and recycle.

The present studies have particularly demonstrated that leachate recycle acts to ensure a high degree of equilization of leachate characteristics, thereby markedly reducing the substantial short-term variations in concentrations of constituents typical of leachate from single contact systems. This attribute permits increased predictability of leachate composition and facilitates improved design and operation of controlled landfill disposal systems. Moreover, leachate recycle accelerates the opportunity for acclimation to possible biological inhibition by reducing shock loadings and enhancing the neutralization of toxic ingredients.

Data from this research have provided additional assurance that such equilibration can be attained. Conductivity, a parameter which depends on both washout of mobile ions and the general evolution of chemical and biological reactions within the columns and leachate, showed very smooth trends with only modest short-term variations. Moreover, the strong correlations of zinc concentration with pH and ArOH virtually assured that virtual equilibrium between the liquid and solid phases had been achieved for this constituent and, by implication, that equilibrium with other solid phase systems was also enhanced. Therefore, the value of leachate recycle was augmented not only by its ability to promote and sustain consistency in leachate characteristics, but by its role in providing an environment more susceptible to didactic and predictive analysis.

SUMMARY AND CONCLUSIONS

The containment, collection and recycle of

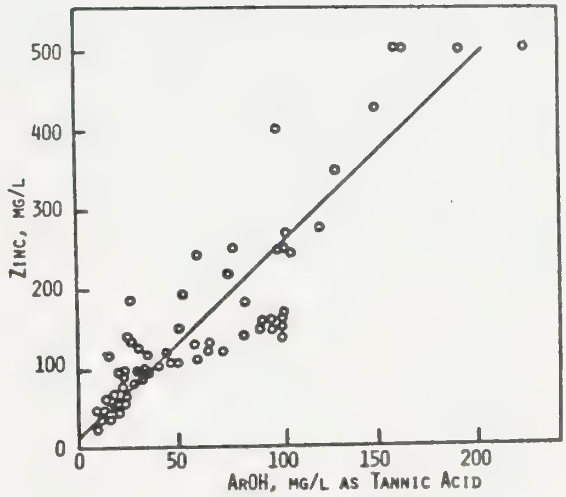

Figure 8. Concentration of Zinc as a Function of Aromatic Hydroxyl Concentration.

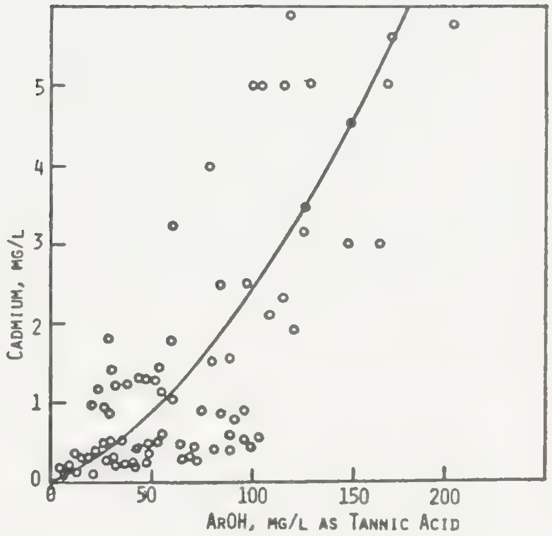

Figure 9. Concentration of Cadmium as a Function of Aromatic Hydroxyl Concentration.

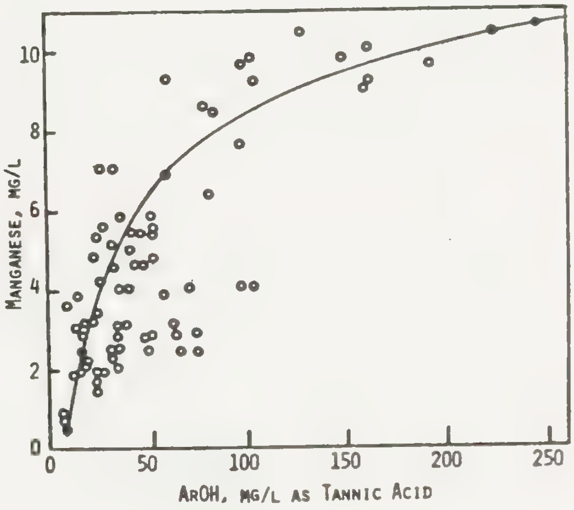

Figure 10. Concentration of Manganese as a Function of Aromatic Hydroxyl Concentration.

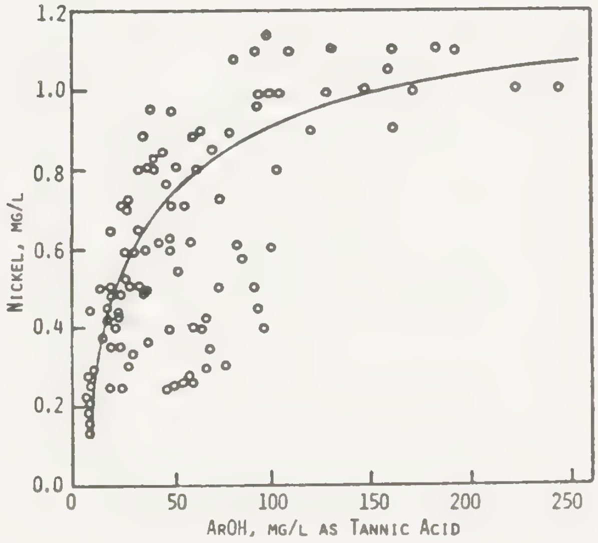

Figure 11. Concentration of Nickel as a Function of Aromatic Hydroxyl Concentration.

landfill leachate has been shown to substantially enhance homogeneity with respect to the biological and chemical processes occurring within the solid waste mass and leachate. In addition, promotion of such homogeneity can significantly moderate the normal short-term and long-term variations typical of landfill systems without leachate recycle. As a consequence, an improved degree of both immediate and extended predictability of leachate properties is possible, thereby facilitating plans for design and operation of landfills and associated leachate management systems.

The reactivity and fate of heavy metals in leachates and their potential for adverse environmental impact were determined to be dependent upon an understanding of solubility equilibria operative under defined environmental conditions. Heavy metal concentrations in the leachates were found to be indicative of the attainment of solubility equilibrium with the metal sludges used and codisposed with residential-type solid wastes. Solubility data, combined with the persistence of low levels of dissolved sulfides, were confirmatory evidence of a sulfide precipitant control mechanism, modified to some degree by the presence of other complexing influences. Strong correlations of dissolved zinc, cadmium, nickel and manganese levels with the concentrations of aromatic hydroxyl groups in the leachates provided important evidence that the major supplemental complexing effect was likely due to the presence of humic substances and tannins in the leachate. These latter results were consistent with humic substances-heavy metal interactions reported elsewhere.

The demonstration of fundamental sulfide control of heavy metals in leachates, even when exposed to heavy metal inhibition of associated microbially mediated processes, provided additional assurance that, with very few exceptions, co-disposal of heavy metals with residential-type solid wastes can be an effective technique for accommodating limited quantities of such materials. The results of this research should lead to a better understanding of this process and a determination of heavy metal loadings that can be safely included in landfill disposal operations. Of the heavy metals available in the plating sludge employed during this research, only zinc exhibited high concentrations in the leachate and only briefly during early phases of stabilization. therefore, provided that the microbially mediated processes necessary for production of sulfides and other species are not impeded by heavy metal toxicity, metals such as Cu, Cd, Pb, Zn, Ni, and Fe should be effectively removed by precipitation and filtration as metal sulfides, particularly when managed with leachate containment and recycle. Moreover, due to the highly confining nature of most landfills, such removal should be relatively permanent and thereby should help alleviate long-term closure concerns.

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